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Treatment of Municipal Waste Water by Photocatalytic Method

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Abstract In this study, the semiconductor photocatalytic disinfection of secondary treated municipal wastewater was investigated. Natural water from a spring in Ethiopia prefecture, which is used for the water supplies for the city of Ethiopia, Crete, and samples from the effluents of the secondary settling tank of the municipal wastewater treatment plant of Ethiopia were collected. The samples were exposed to UV-A irradiation in the presence of TiO_2. The parameters examined in this study were the length of TiO_2 / UV-A treatment for effective disinfection, the microorganism type (total coliforms, enterococci), the relative bactericidal activity of three different types of TiO_2, the amount of the catalyst needed, and the pH of the samples. The results presented here show that commercial TiO_2 powder Degussa P25 is the most effective catalyst of the three used. *Enterococci* showed a stronger resistance to photocatalytic disinfection, whereas small pH changes do not seem to have a significant effect on it.

Keywords: *semiconductor photocatalysis, water, wastewater, disinfection*

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1. Introduction

Several environmental issues, with the most important ones the continuous decrease of the available water for human and agricultural use as well as the increase of hazardous wastes and the atmospheric contamination have marked the research on the development and application of methods and technologies for remediation of air, soil and water as a hot topic. Among other achievements, this research has resulted in the development of the so called Advanced Oxidation Processes (AOPs) which have been defined "as those which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification" [1]. Hydroxyl radical ($OH^{\bullet}$), is a very strong oxidizing species with a redox potential of 2.8 V, capable of rapid oxidation of a large number of pollutants and of molecules of cell walls of microorganisms [2,3,4]. Hydroxyl radicals can be generated by several processes, such as combinations of ozone, hydrogen peroxide and UV radiation, heterogeneous photocatalysis, (i.e. TiO_2 / UV-A), ozonation at high pH, combination of ozone and ultrasound, etc [3,5,6,7]. Heterogeneous photocatalysis involves the transfer of an electron from the valence band to the conductance band of a semiconductor molecule, like TiO_2, through excitation by a photon in the UV region. In order for this transfer to occur, the energy of the photon must be equal or higher of the band gap energy (E_{bg}) of the semiconductor. Consequently, a very reactive electron – positively charged hole pair (e^- - h^+) is formed. In the absence of redox reactive molecules in the close environment of the semiconductor, a recombination process will take place and the energy of the absorbed photon will be dissipated as heat. If, however, redox reactive species are present, then both e^- and h^+ can react with them in a series of oxidation / reduction reactions [5,6]. These processes are schematically represented in Figure 1, which shows the photocatalytic formation of hydroxyl and superoxyl radicals. The mechanisms which are involved in the degradation and disinfection reactions occurring in environmental samples during advanced oxidation processes are the center of intensive research [2,4,5,8,9]. In any case, AOP in general and heterogeneous catalysis in particular become more and more important means for the scientists to confront environmental problems.

In the work presented here, we studied the TiO_2-assisted photocatalytic disinfection of natural water samples collected from kombolcha city of Ethiopia, and wastewater samples collected from the effluents of the secondary settling tank of the municipal wastewater treatment plant. Two groups of microbial organisms, one gram-negative (total coliforms), and one gram-positive (enterococci) were used in order to elucidate the bactericidal efficiency of three different types of commercial TiO_2 products, namely Degussa P25 (80% Anatase, 20% Rutile), Tronox HP_2 (100% Rutile) and Millennium PC_{500} (100% anatase). The effects of other parameters, like the duration of the irradiation, the pH and the amount of the catalyst on the bactericidal activity were also examined.

2. Materials and Methods

2.1. Sample Collection

Natural water: samples were collected from the surface water of the little pond at the outflow of Kombolcha city of Ethiopia. A 5 L container was used for sample collection, which was previously rinsed twice with a diluted HCl solution, (~1 N), and then rinsed thoroughly with freshly prepared deionized water. Finally, the container was rinsed twice with sterile water. **ii**. Secondary treated municipal wastewater: samples were collected from the effluent of the secondary settling tank of the municipal wastewater treatment plant of Ethiopia in sterile 0.5 L bottles. The samples were transferred to the laboratory immediately after collection, for photocatalytic treatment.

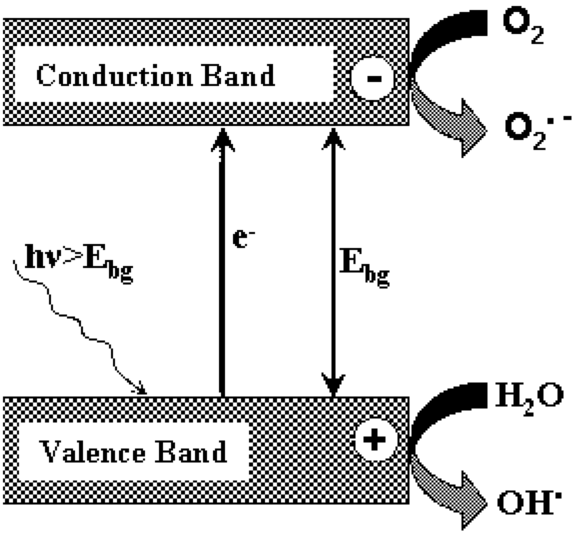

Figure 1. Schematic representation of the formation of the redox active electron – hole pairs at the surface of TiO_2. Subsequently, electrons and positively charged holes react with redox active species in the solution to form very reactive radicals

2.2. TiO_2 / UV-A Disinfection

300 mL of sample was transferred to a glass container in which a smaller glass cylinder was centered (Figure 2). A UV-A lamp (Radium Ralutec 9 W, UV-A 350-400 nm) was positioned in the cylinder so that the whole volume of the sample was irradiated by the UV light. Just before illumination, appropriate amount of TiO_2 powder was added to the sample container. Three different brands of TiO_2 were tested: Degussa P25 (80% Anatase, 20% Rutile), Tronox HP_2 (100% Rutile) and Millennium PC_{500} (100% Anatase). In order to keep the catalyst suspended in the sample body, a magnetic stirrer was used.

2.3. Microbiological Analysis

0.25 mL of the sample-TiO_2 suspension was spread over the appropriate nutrient agar in Petri dishes. Total coliforms and enterococci were determined as colonies on Membrane Lauryl Sulphate Broth containing 1.5 % Agar No 1 (Lab M, UK), and Slanetz & Bartley Medium (Lab M, UK), respectively. The Petri dishes were incubated at 37 °C for 24 h and 48 h, and the numbers of colonies were counted. An alternative method, which included removal of TiO_2 by Buchner filtration after photocatalytic treatment and subsequent filtration of the cells on a sterile cellulose ester membrane, (Gelmann, USA), was found to be inappropriate due to the strong adsorption phenomena of the cells on the TiO_2 surface.

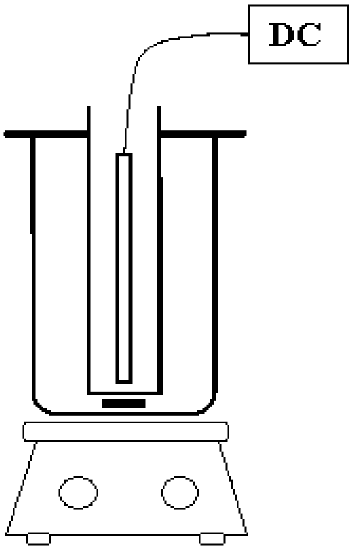

Figure 2. The laboratory-made reactor for TiO_2 / UV-A disinfection of natural water and wastewater

3. Results and Discussion

3.1. Relative Bactericidal Activity of Three Different TiO_2 Catalysts

The survival of total coliforms and enterococci (CFU/mL) in natural water and wastewater samples irradiated by UV-A light for 0, 15, 30, 45 and 60 min is presented in Figure 3, and, as a percentage of the cells in untreated samples (blanks) in Table 1 and Table 2. With this set of experiments, the relative effectiveness of the three catalysts used (Degussa P25, Trolox HP_2 and Millennium PC_{500}) was to be determined. Degussa P25 shows a higher bactericidal activity for both groups of microorganisms examined, as compared to the other two catalysts for both natural water and wastewater samples. The bactericidal activity of Tronox and Millennium TiO_2 was similar for total coliforms, whereas Tronox seemed to be slightly more efficient for enterococci killing, as compared to Millenium. Experiments with 48h of incubation showed similar results (data not shown). These results are in good agreement with previous studies showing a better behaviour of Degussa P25 as a photocatalyst as compared to other types [10,11,12]. This phenomenon has been attributed to "electron jumping" from the conduction band of anatase part to the rutile part of the TiO_2 crystal, thus stabilizing the e^- - h^+ pair [13]. The other two types of TiO_2 are pure anatase and rutile, so such stabilization processes cannot occur in their crystals.

3.2. Effect of TiO_2 Load on Wastewater Disinfection

Two different loads of the Degussa P25 TiO_2 catalyst were tested regarding the microorganisms survival after certain time periods of irradiation. The results of these experiments are shown in Figure 4 and in Table 3. 2-fold increase of the catalyst load results in significant increase of bactericidal activity. This is more profound for enterococci experiment where one can see that increase of TiO_2 load from 0.5 to 1 g/L decreases the survival from 78 % to 35 % after 15 min of irradiation. When 1 g/L of Degussa P25 TiO_2 was used, the total coliforms were reduced to 16% and to 3% after 15 min and 60 min of irradiation, respectively. From these results we can conclude that for our irradiation conditions and for the specific samples we tested, there is no saturation of the photocatalytic activity when 0.5 g/L of Degussa P25 TiO_2 was used.

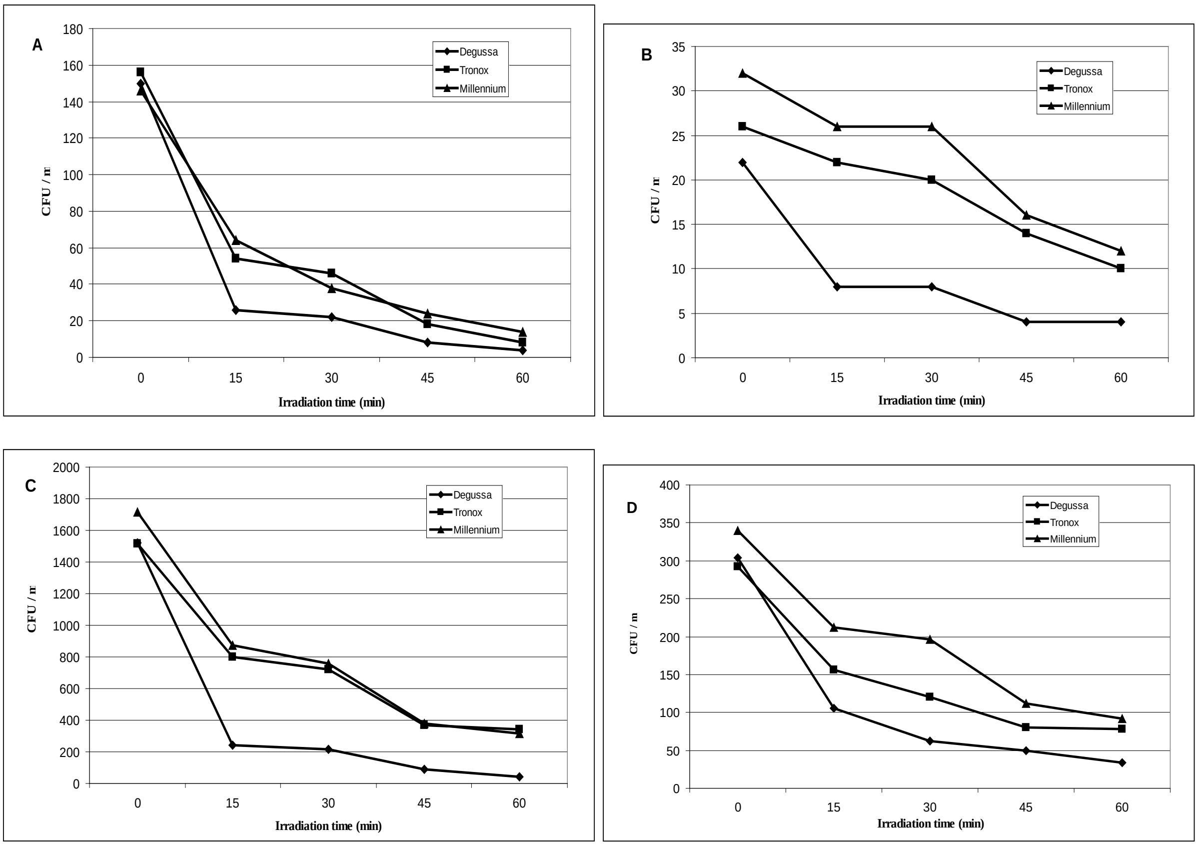

Figure 3. Bactericidal activity of Degussa P25, Trolox HP_2 and Millennium PC_{500} TiO_2 catalysts. Natural water from Kalamionas spring (A, and B) and secondary treated municipal wastewater (C and D) were irradiated by UV-A light, in the presence of the catalysts, for 0, 15, 30, 45 and 60 min. The survival of total coliforms (A and C) and enterococci (B and D) is expressed as colony forming units per mL of treated sample (CFU/mL).

Table 1. Survival of total coliforms and of enterococci after TiO_2 / UV-A photocatalytic treatment of Kalamionas spring natural water as a percentage of the cells in an untreated sample (cells were cultivated for 24h at 37°C). Three different catalysts (1 g/L) were used.

Irradiation time (min)	Total Coliforms Survival (%)			Enterococci Survival (%)		
	Degussa	Tronox	Millennium	Degussa	Tronox	Millennium
0	100	100	100	100	100	100
15	17	35	44	36	85	81
30	15	29	26	36	77	81
45	5	12	16	18	54	50
60	3	5	10	18	38	38

Table 2. Survival of total coliforms and of enterococci after TiO_2 / UV-A photocatalytic treatment of secondary treated municipal wastewater as a percentage of the cells in an untreated sample (cells were cultivated for 24h at 37°C). Three different catalysts (1 g/L) were used.

Irradiation time (min)	Total Coliforms Survival (%)			Enterococci Survival (%)		
	Degussa	Tronox	Millennium	Degussa	Tronox	Millennium
0	100	100	100	100	100	100
15	16	53	51	35	53	62
30	14	48	44	20	41	58
45	6	24	22	16	27	33
60	3	23	18	11	27	27

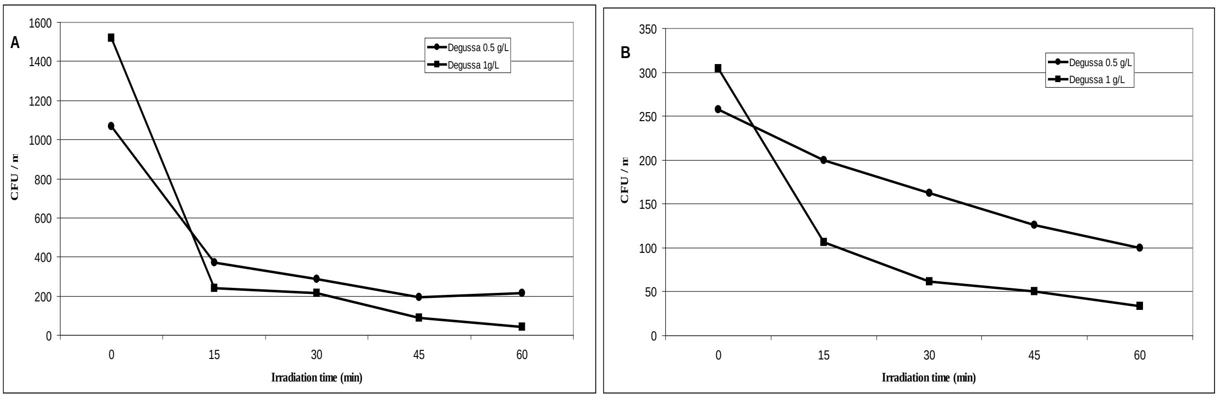

Figure 4. Bactericidal activity (expressed as CFU/mL) of 0.5 g/L (■), and 1 g/L (●) Degussa P25 TiO_2 for total coliforms (A) and for enterococci (B) after TiO_2 / UV-A treatment.

The results presented in 3.1 and in 3.2 show, at least for our experimental conditions, a much stronger resistance of enterococci to photocatalytic disinfection as compared to total coliforms. The origin of this difference can be attributed to the differences on the cell wall structures of these two types of microorganisms: total coliforms, as gram-negative cells, have a much thinner peptidoglycan layer in the cell wall compared to the peptidoglycan layer in the cell wall of enterococci, which is a gram-positive cell. These results are in agreement with previous studies, in which similar differentiation regarding resistance to photocatalytic destruction between gram- positive and gram-negative bacteria has been shown [14].

3.3. ph Effect on Photocatalytic Bactericidal Activity

Potential changes on the bactericidal activity of TiO_2 due to slight changes of the pH of the samples were investigated for three pH values: 6, 7 and 8. 1 g/L Degussa P25 TiO_2 was used and the samples were irradiated for 0, 15, 30, 45 and 60 min, as described in Materials ans Methods. Figure 5 presents the results of these experiments. In general, the changes of the pH values of the samples caused small alterations of microorganisms' survival, some of which may include more complex kinetic parameters (for example see the difference in the kinetics of enterococci survival at pH 7 and pH 8, Figure 5 B). In any case, more experiments are needed in order to elucidate possible correlations between pH and photocatalytic disinfection activity.

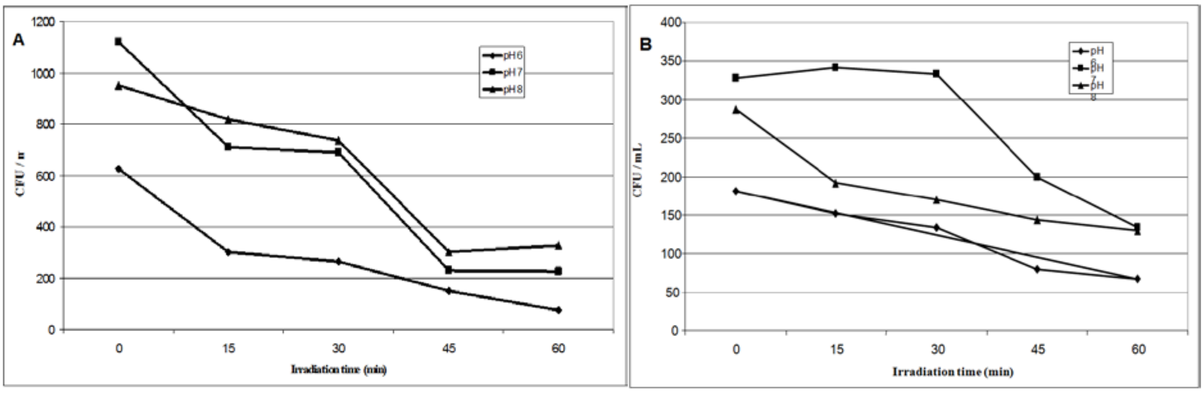

Figure 5. pH effects on the survival of total coliforms (A) and of Enterococci (B). 1 g/L of Degussa P25 TiO_2 was used.

4. Conclusion

It was concluded that photocatalytic method is suitable for treatment of municipal wastewater. The results are in good agreement with Degussa P25 as a photocatalyst and attributed to "electron jumping" from the conduction band of anatase part to the rutile part of the TiO_2 crystal. The loading of TiO_2 in waste water is similar differentiation regarding resistance to photocatalytic destruction between gram- positive and gram-negative bacteria. The possible correlations between pH and photocatalytic disinfection activity generated.

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